MTL TR 87-45

AD

AD-A189 196

FLUORESCENCE ENHANCEMENT IN A POLYURETHANE CONTAINING AN ORGANIC DYE

ORNA I. KUTAI and SAMUEL J. HUANG
THE INSTITUTE OF MATERIALS SCIENCE
UNIVERSITY OF CONNETICUT

CATHERINE A. BYRNE
POLYMER RESEARCH DIVISION

EDWARD J. POZIOMEK
CHEMICAL RESEARCH DEVELOPMENT AND ENGINEERING CENTER

September 1987

Approved for public release; distribution unlimited.

US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY
LABORATORY

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER MTL TR 87-45	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER A189196	
4. TITLE (and Subtitle) FLUORESCENCE ENHANCEMENT IN A POLYURETHANE CONTAINING AN ORGANIC DYE	5. TYPE OF REPORT & PERIOD COVERED Final Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Orna I. Kutai,* Samuel J. Huang,† Catherine A. Byrne, and Edward J. Pozlomek‡	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 SLCMT-OMP	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 20783-1145	12. REPORT DATE September 1987
	13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

(SEE REVERSE SIDE)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Fluorescence
Polyurethanes
Azine fluorescence
Detection
~~DIPAIN~~

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(SEE REVERSE SIDE)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 18

SUPPLEMENTARY NOTES

*Present address: Union Carbide Corporation, Specialty Chemical Division, Old Saw Mill Road, Tarrytown, New York 10591.

†Present address: The Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06268

‡Present address: Research Directorate, Chemical Research Development and Engineering Center, Aberdeen Proving Ground, Maryland 21010

Block No. 20

ABSTRACT

Transparent polyurethane sheets have been prepared containing a dispersed or covalently bonded organic dye. The fluorescent dyes are 2-diphenylacetyl-1,3-indanedione-1-*p*-dimethylaminobenzaldazine or the *p*-dihydroxyethylamino-benzaldazine analog, which can be called DIPAIN derivatives. Changes in the fluorescence of the dyes have been studied in the presence of methyl benzilate and several nonvolatile aliphatic alcohols. When methyl benzilate is added during polymerization, fluorescence in both dye-containing sheets increases, but the effect is greater for the sheet containing the covalently bonded dye. When a solution of methyl benzilate is dropped on the surfaces of the dye-containing sheets, the effect is greater for the dispersed dye. The dimethyl dye blooms to the surface of the polyurethane sheet and can be wiped off as a fine orange powder. Decyl alcohol shows an enhancement effect when spotted together with the dimethyl dye on a silica gel TLC plate. Fluorescence enhancement is also observed when a polyurethane sheet containing dimethyl dye is placed in contact with decyl alcohol vapor. The nature of the interaction can include the aromatic ring systems of the dye and methyl benzilate, and also the interaction of the dye with decyl alcohol through hydrogen bonding.

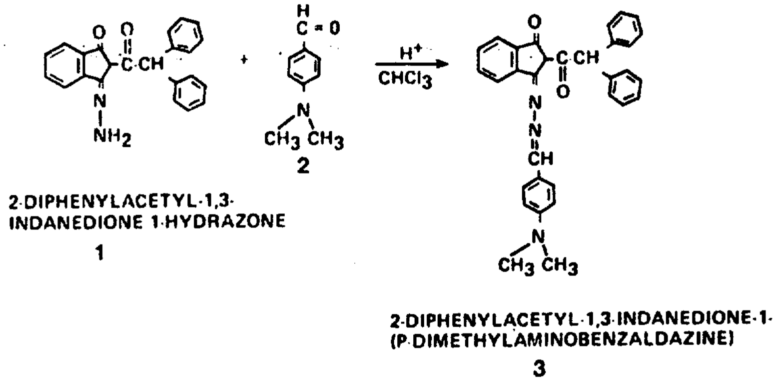
(Keywords:

CONTENTS

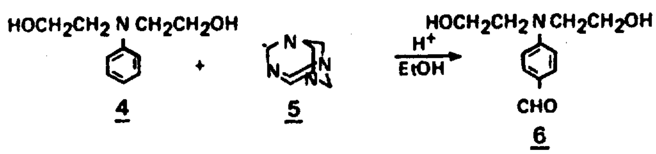
INTRODUCTION

This research investigated molecular complex formation of fluorescent dyes and dye-containing polyurethanes with aromatic and aliphatic organic compounds. Molecular complex formation between members of a class of fluorescent 1,3-indanedione-1-imine derivatives and α-amino acids, α-hydroxy acids, esters of α-hydroxy acids, insecticides, and herbicides on solid supports, such as glass fiber paper and silica, has been reported.[1,2]

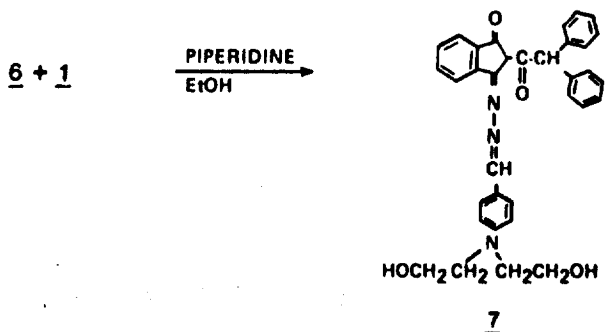
Complex formation was found to alter the fluorescence behavior of the dyes either by effecting more intense fluorescence or by shifting the fluorescence spectrum, thus permitting detection of the complex. Of the dyes evaluated by Poziomek et al,[1,2] 2-diphenylacetyl-1,3-indanedione-1-p-dimethylaminobenzaldazine exhibited the strongest fluorescence and displayed the least specificity; i.e., it formed a complex with the greatest number of organic compounds, including methyl benzilate.



(1)



(2)



(3)

1. POZIOMEK, E.J., CRABTREE, E.V., and MULLIN, J.W. *Fluorescence Detection of Specific Insecticides, Rodenticides, Herbicides and Fungicides*. Anal. Lett., v. 14, no. A11, 1981, p. 825.
2. POZIOMEK, E.J., CRABTREE, E.V., and MacKAY, R.A. *Reagents for the Detection of α-Hydroxy Acid Esters*. Anal. Lett., v. 13, no. A14, 1980, p. 1249.

This study examined the fluorescence effect of several organic compounds on dye 3, its functionalized analogue, 2-diphenylacetyl-1,3-indanedione-1-p-bis(2-hydroxyethyl) aminobenzaldazine 7, and dye 3- and dye 7-containing polyurethanes. Dye 3 was dispersed within the polyurethane matrix, while 7 was covalently bonded to it.

The proclivity of the benzaldazine dyes to form molecular complexes, which can be identified fluorometrically, permits using the dyes in chemical substances detection applications. Incorporation of the dyes into polymers renders them more useful for two reasons. A smaller amount of dye is required when it is incorporated into a polymer matrix, and these highly amorphous polymers are capable of being fabricated into clear coatings.[3]

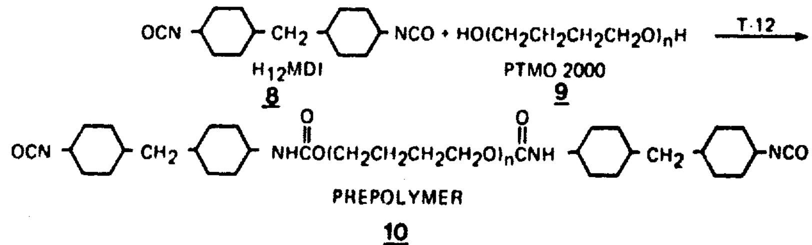
EXPERIMENTAL

Dye Synthesis

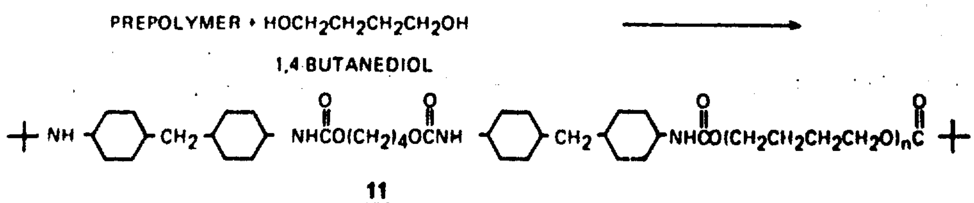
The synthesis of dye 3,[4] outlined in Equation (1), and dye 7,[5,6] outlined in Equations (2) and (3), have been described previously.

Polyurethane Synthesis

Polyurethanes 11, based on methylene bis(4-cyclohexyl isocyanate) 8(H_{12}MDI) (Desmodur W, Mobay Chemical Corporation), were synthesized by the two-step prepolymer method. The soft segment component was poly(tetramethylene oxide) (PTMO) 9 of molecular weight 2000 (Polymeg 2000, Chemicals Division, The Quaker Oats Company). The prepolymer 10 resulting from the reaction of 8 with 9 (Equation 4) was chain extended with 1,4-butanediol (Equation 5). The molar ratio of the reactants was



(4)



(5)

3. BYRNE, C.A., MACK, D.P., and SLOAN, J.M. *A Study of Aliphatic Polyurethane Elastomers Prepared From Diisocyanate Isomer Mixtures*. Rubber Chemistry and Technology, v. 58, 1985, p. 985.
4. BRAUN, R.A., and MOSHER, W.A. *2-Diphenylacetyl-1,3-indanedione 1-Hydrazone - A New Reagent for Carbonyl Compounds*. J. Amer. Chem. Soc., v. 80, 1958, p. 2749; ibid., v. 80, p. 3048.
5. KUTAL, O.I., BYRNE, C.A., POZIOMEK, E.J., SUIB, S.L., and HUANG, S.J. *A Fluorescent Probe of Polyurethane Elastomer Properties*. Org. Coatings Appl. Polym. Sci. Proc., Amer. Chem. Soc., Div. Polymeric Mater. Sci. Eng., v. 49, 1983, p. 254.
6. KUTAL, O.I. *Fluorescence of 1,3-Indanedione-1-Imine Derivatives in Polymer Matrices*. Ph.D. Dissertation, The University of Connecticut, Storrs, Connecticut, 1984.

2.6:1.0:1.5 for Desmodur W:PTMO:1,4-butanediol, which represents an isocyanate-to-hydroxyl ratio of 1.05:1. The reaction was catalyzed by a four percent (mass to volume) dibutyltin dilaurate (T-12, M&T Chemicals) solution in dry methyl ethyl ketone (MEK) (IUPAC:2-butanone). Starting materials 8 and 9 were used as supplied, and 1,4-butanediol was dried over molecular sieves. The polyurethane synthesis has been described previously.[7]

The uncured viscous mixtures were poured into polypropylene molds and compression molded at 100°C under 125 psi (862 kPa). The samples were cured in the press for one hour at 100°C and for fifteen hours in an oven at 100°C. Depending on the mold, films varied in thickness from 58 to 71 mils (0.15 to 0.18 cm). The variation in a single sample was ±1 mil (2.54×10^{-3} cm). Compression-molded samples were cut to measure 3.50 x 0.80 cm.

Dye Incorporation

Dyes 3 and 7 were generally incorporated into the polyurethane matrix by blending into 10 at the point of chain extension, as described previously.[5,6] Dye concentration in the polyurethanes was 2.2×10^{-7} to 3.7×10^{-6} moles/100 g polymer. Comparisons were made with polyurethanes of the same dye concentrations. In one or two cases mentioned below, 7 was added to diisocyanate 8 prior to prepolymer synthesis.

Fluorescence Spectroscopy

Fluorescence spectra were obtained using a Perkin-Elmer LS-5 scanning spectrophotometer. Samples were held in the front surface accessory. The fluorescence spectra for the dye-containing polymers are shown in Figure 1. The excitation wavelength was 476 nm.

Fluorescence Microscopy

An epi-fluorescence microscope (Olympus Vanox, Japan-Spectra Instruments, Inc., Littleton, MA), powered by a 200-W mercury lamp, was used to try to evaluate the homogeneity of the dye distribution in the polyurethane films. Film samples ranging in thickness from 58 to 71 mils (0.15 to 0.18 cm) were examined while mounted on glass slides. The resolution of the instrument is approximately 0.5 mm. Data were quantified by the Olympus control unit attached to the microscope.

Samples were examined under white light in the transition mode and fluorescent light in the epiluminescent mode. The excitation filter permitted excitation from 480 nm, and it had a peak maximum of 490 nm. Emission was examined at wavelengths higher than 500 nm using another filter. Samples were examined at magnifications ranging from 48 to 1200X.

Treatment With Methyl Benzilate, An Aromatic Compound

The polyurethane samples were treated with methyl benzilate 12 in one of three ways: 1) adding 12 as a solution in THF to the prepolymer 10 during polymerization at the chain extension step; 2) immersion of the polyurethane 11 in an ethanolic

7. BYRNE, C.A., McHUGH, E.A., MATTON, R.W., and SCHNEIDER, N.S. *Preparation and Properties of Polyurethane and Polyurethaneurea) Elastomers From Methylene Bis(4-cyclohexylisocyanate)*. Org. Coat. Appl. Polym. Sci. Proc., Amer. Chem. Soc., Div. Org. Coat. Plastics Chem., v. 47, 1982, p. 49.

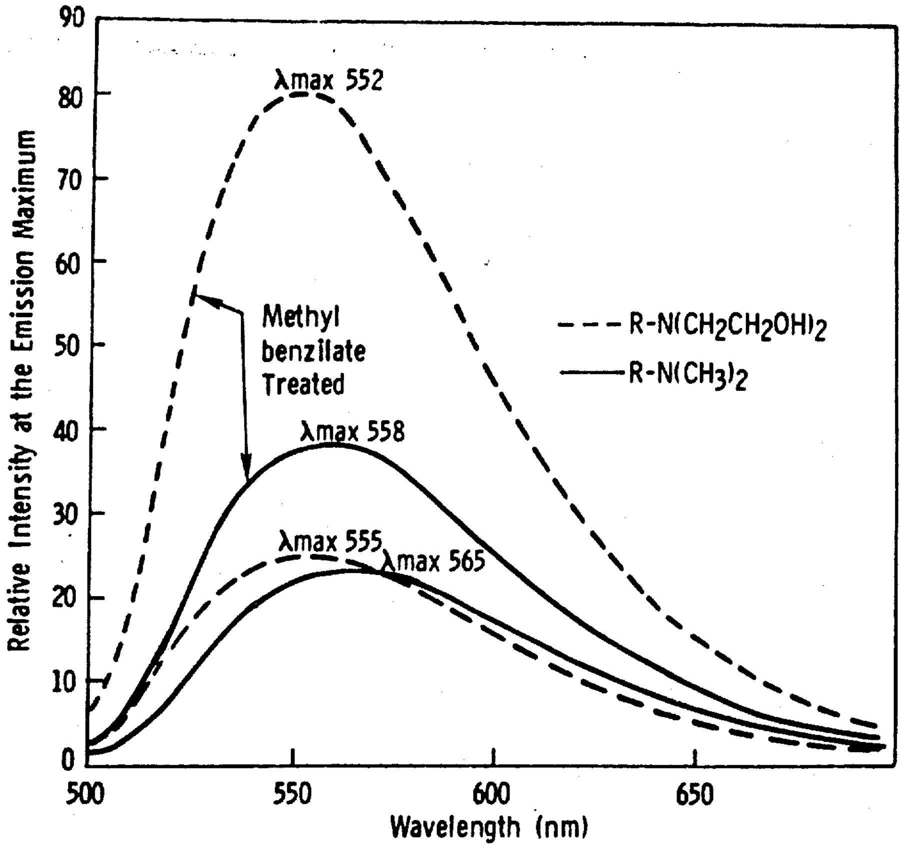
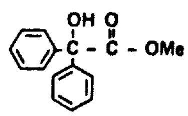


Figure 1. Effect of methyl benzilate treatment of polyurethanes in which dye is dispersed and to which dye is covalently bonded. Dye concentration: 3.67×10^{-6} moles/100 g polymer. Methyl benzilate concentration: 2.06×10^{-5} moles/100 g polymer. (---) bonded dye 7; (—) dispersed dye 3.

solution of 12; or 3) adsorption of an ethanolic solution of 12 onto the polyurethane surface. In all cases, the concentration of 12 exceeded that of the dyes by at least one order of magnitude. Generally, four specimens of each sample were tested. Methyl benzilate was used, because it has been shown to exhibit a very strong fluorescent enhancement with 3 on solid supports such as silica gel.[2]



12

When 12 was added during polymerization, the dyes were added to 10 at the same time. For the immersion tests, 3 was added to 10 during chain extension, and 7 was added to 8 prior to prepolymer synthesis. For the adsorption test, 7 was added at different stages in different polyurethane samples, and 3 was added to 10 during chain extension.

Treatment With Aliphatic Compounds

The interaction between dyes 3 and 7 and the following aliphatic compounds was investigated: 2-dibutylaminoethanol (2-DBAE), diethylene glycol monobutyl ether

(DEGE) [IUPAC:2-(2-butoxyethoxyethanol)], and n-decyl alcohol (DA) [IUPAC:1-decanol]. These compounds were distilled and used both neat and as one percent solutions in ethanol. The enhancement effect was studied in three ways: 1) diffusion (immersion) in dye 7-labeled polyurethane; 2) interaction in the solid state (silica gel) with 3 and 7; and 3) vapor phase diffusion (sorption) of DA in dye 3-containing polyurethane.

The diffusion of DA into a 0.21072-g polyurethane specimen, in which 3 was dispersed, took place under vacuum. Sorption measurements were conducted at 25°C using an electrobalance. Mass increase due to solvent uptake was monitored over time with a strip-chart recorder. DA has a saturation vapor pressure P_0 = 0.05 mm Hg (≈7 Pa). This value was determined using Antoine's equation with appropriate coefficients[8] and confirmed by extrapolation of the line obtained from plotting known values.[9] The sorption procedure, which took eight days due to low vapor pressure of DA, involved equilibrating the film with solvent at a value approaching unit activity. A schematic diagram of the sorption apparatus is shown in Figure 2.

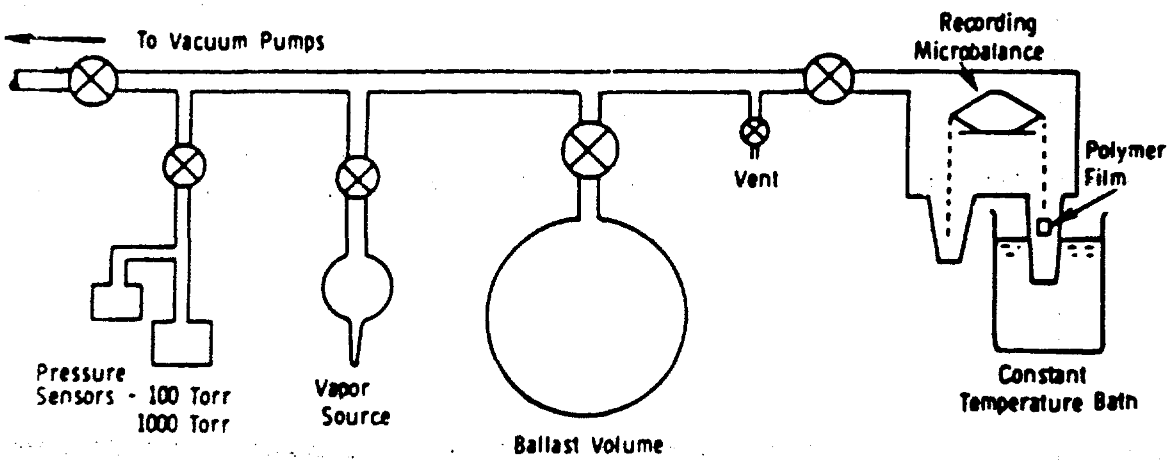


Figure 2. Vapor sorption apparatus.

RESULTS AND DISCUSSION

Treatment With Methyl Benzilate 12, an Aromatic Compound

Method 1: Treatment With Methyl Benzilate 12 During Polymerization

Fluorescence enhancement in the presence of 12, which had been observed in the crystalline state on solid supports,[1,2] has been found to occur in polymer matrices. The enhancement effect observed with 3 and 7 when 12 was added to the prepolymer is represented by the curves in Figure 1.

Compound 12 effected a 65 percent increase in fluorescence intensity in the dye 3-containing sample and a 225 percent increase in the sample containing 7 (Table 1). The fluorescence enhancement realized by the latter was visible to the unaided eye.

8. *CRC Handbook of Chemistry*, 51st Ed., R.C. Weast, ed., The Chemical Rubber Co., Cleveland, Ohio, 1970, p. C-268.
9. *The Merck Index*, 9th Ed., M. Windholtz, ed., Merck and Co., Inc., Rahway, New Jersey, 1976, p. 198.

Table 1. FLUORESCENCE ENHANCEMENT IN POLYURETHANES TREATED WITH METHYL BENZILATE DURING POLYMERIZATION

Sample	Fluorescence Intensity Increase After Exposure (%)
11/3	65
11/7	225

The dramatic fluorescence enhancement observed in the dye 7-labeled polyurethane suggests that complex formation is favored when the dye is covalently bonded. Dye conformation may be altered by covalent bonding such that 12 has greater access to the covalently bonded dye 7 than to the dispersed dye 3. The distributions of 3,7 and methyl benzilate in the hard and soft segments also probably affect the result. While 7 is covalently bonded and assumed to be present in the hard segment, it could be bonded in very short, hard segments that might be phase mixed.

Method 2: Treatment by Immersion

Two samples, one containing 3 and one labeled with 7, were treated with a one percent (by weight) solution of 12. Dyes 3 and 7 were present in concentrations of 4.05×10^{-7} and 3.05×10^{-7} mol/100 g, respectively. Specimens were weighed before immersion and after drying in order to ensure the absence of residual solvent. Specimens were dried under ambient conditions.

Fluorescence enhancement occurred in the methyl benzilate-exposed samples. Typical data for specimens exposed to 12 for at least four days and dried for seven days are listed in Table 2.

Table 2. FLUORESCENCE ENHANCEMENT IN POLYURETHANES IMMERSED IN METHYL BENZILATE SOLUTION

Sample	Fluorescence Intensity Increase After Exposure (%)
11/3	4069
11/7	9

The fluorescence intensity increase for 11 containing 3 is far larger than for the polymer containing 7. While these data represent the reverse of the trend observed for samples treated during polymerization (Method 1), they are entirely reproducible. This reverse trend indicates that 3 is more accessible to 12 than 7 in the immersion test. This is not surprising, since 3 continually bloomed as a fine orange powder on the surface of the transparent polyurethane sheet starting several days after it was prepared. The immersion solvent showed evidence of dissolved dye. Dye 7 is covalently bonded in the polyurethane hard segment, which is typically less swellable by common solvents. The solution of methyl benzilate simply did not come

in contact with 7 to any extent. Ethanol was chosen as the solvent for these immersion tests, because the swelling of the polymer was low in this solvent and the integrity of the sample was maintained. The weight uptake after 66 hours immersion of the polyurethane in pure alcohol was 72%, compared with 226% in tetrahydrofuran and 1300% in methylene chloride.

Method 3: Treatment by Adsorption

Methyl benzilate was adsorbed onto polyurethane by placing 12, as a one percent solution, dropwise on the film surface. After solvent evaporation, the samples were wiped with 2-propanol to remove 12, which may have crystallized on the polymer surface. Fluorescent enhancement was realized in both the covalently bonded and dye-dispersed systems. The intensity was so great as to surpass the measuring capability of the instrument for samples whose dye concentration was 10^{-6} mol/100 g.

Three polyurethane samples in the 10^{-7} mol/100 g dye concentration range were treated with a one percent solution of 12. These polyurethanes were prepared with dye as follows: 1) Dye 7 added to 8 prior to prepolymer synthesis at a concentration of 2.19×10^{-7} mol/100 g; 2) Dye 7 added to 10 at the chain extension step, resulting in 7 bonded to hard segment at a concentration of 2.19×10^{-7} mol/100 g; and 3) Dye 3 added at the chain extension step dispersed within the matrix at a concentration of 3.67×10^{-7} mol/100 g.

The samples were permitted to dry for one day before their fluorescence was measured. Sample 3 exhibited the greatest fluorescent enhancement following exposure to 12. The fluorescence intensity increase of 92% for sample 3 was followed by an increase of 17% for sample 1, which was followed by an increase of 2 percent for sample 2 (Table 3). The enhancement difference between samples 1 and 2 may not be significant; however, the difference between samples 3 and either samples 1 or 2 is significant.

Table 3. FLUORESCENCE ENHANCEMENT IN POLYURETHANE SURFACE-TREATED WITH METHYL BENZILATE

Sample Number	Fluorescence Intensity Increase (%)
1	17
2	2
3	92

These data suggest that the dispersed dye is more accessible to 12 than the bonded dye. This may be due either to migration of 3 to the sample surface (blooming) or more accessible internal location of the dispersed dye as compared to that of the bonded dye. While 3 is presumed to be dispersed evenly throughout the polyurethane matrix (assuming no migration), it may be located primarily in the soft segment domains, the reason being that the soft segment comprises 71% of the matrix. Soft segments are generally more permeable to and swellable in organic solvents than polyurethane hard segments. Selective sorption ofthe methyl benzilate solution into the soft segment would lead to the greatest degree of fluorescence enhancement to be

realized by sample 3. This relationship between the nonfunctionalized and functionalized dyes where the dispersed dye realized the greater fluorescence enhancement is similar to that observed in the samples exposed to 12 by immersion.

Samples 1-3 were rescanned ten days after the initial data were collected. The results are shown in Table 4. The increase in fluorescence enhancement with time for all samples may be due to loss of polymer-free volume within the matrix due to evaporation of ethanol that had diffused into the polyurethane upon treatment with methyl benzilate.

Table 4. FLUORESCENCE ENHANCEMENT IN POLYURETHANES SURFACE-TREATED WITH METHYL BENZILATE SOLUTION (RESCANNED AFTER 10 DAYS)

Sample Number	Fluorescence Intensity Increase (%)
1	118
2	90
3	407

In both the immersion and adsorption studies, methyl benzilate effected greater enhancement of dye 3 as compared to 7 regardless of the location of 7. Only in the case where 12 was added directly to the polymerization during chain extension did 8 effect a greater enhancement of 7, which was added at the same time. For an application in which the polymer sheet might be used in chemical detection equipment, the use of non-bonded dye is clearly indicated.

Treatment With Aliphatic Compounds

The fluorescence enhancement effect has been shown to occur with a small number of aliphatic compounds.* Since aliphatic compounds are less likely to form charge-transfer complexes than aromatic compounds, it was appropriate to study fluorescence enhancement in the polymer sheets with aliphatic compounds. This would provide evidence for the general utility of the polymer sheets in detection applications. The aliphatic compounds chosen are all large alcohols; therefore, hydrogen bonding also plays a role in the enhancement effect to be described.

Method 1: Treatment by Immersion

Polyurethane samples containing 7, which were exposed to 2-DBAE, DEGE, and DA for 64 hours in ethanol solution, were scanned in the spectrophotometer six days after exposure. Decreases in fluorescence were observed (Table 5). These decreases, also observed for samples exposed to the neat aliphatic compounds (Table 6), may be due to fluorescence quenching by the aliphatic compounds or to altered morphology as a result of polymer swelling. A polyurethane containing 3 was not studied by this method, but might give a more positive result such as that obtained when methyl benzilate was used.

*ASHMAN, W.P. Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, Maryland, unpublished results.

Table 5. EFFECT OF ALIPHATIC COMPOUNDS (SOLUTIONS) ON FLUORESCENCE OF DYE 7-LABELED POLYURETHANES

Treatment	Fluorescence Intensity Increase (%)
2-DBAE	-70
DEGE	3
DA	-17

Table 6. EFFECT OF ALIPHATIC COMPOUNDS (NEAT) ON FLUORESCENCE OF DYE 7-LABELED POLYURETHANES

Treatment	Fluorescence Intensity Increase (%)
2-DBAE	-92
DEGE	-37
DA	-48

Method 2: Treatment on a Solid Support

The enhancement effect of these aliphatic compounds on 3 and 7 was reexamined in the solid state. Both dyes were immobilized on silica gel-covered thin layer chromatography plates. Enhancement was evident with both 3 and 7. DA effected the greatest enhancement for both dyes. 2-DBAE and DEGE effected fluorescence enhancement to a lesser degree but approximately equal to each other. The aromatic methyl benzilate 12 caused the least enhancement on the silica TLC plates. Based on these data, sorption was conducted with DA.

These data are significant, because they indicate that the mechanism of fluorescence enhancemnt is not exclusive to interaction between aromatic rings. The interaction may be that of charge transfer; however, DA is also capable of hydrogen bonding interaction with both dyes. The interaction between 12 and the dyes may also include hydrogen bonding.

Method 3: Treatment by Vapor Sorption

The polyurethane specimen realized a 6.5 percent mass increase due to sorption of DA. The sorption data are plotted as weight uptake versus the square root of time (Figure 3) and display essentially Fickian diffusion behavior. At the activity of the system, the average diffusion coefficient was calculated as having a value of 1.1285×10^{-8} cm^2/sec. Sample fluorescence intensity increased 35% as a result of association with DA, indicating a significant interaction with the dye 3-containing polyurethane matrix. The sorption experiment simulates the exposure of chemical detection equipment to toxic vapors in the environment.

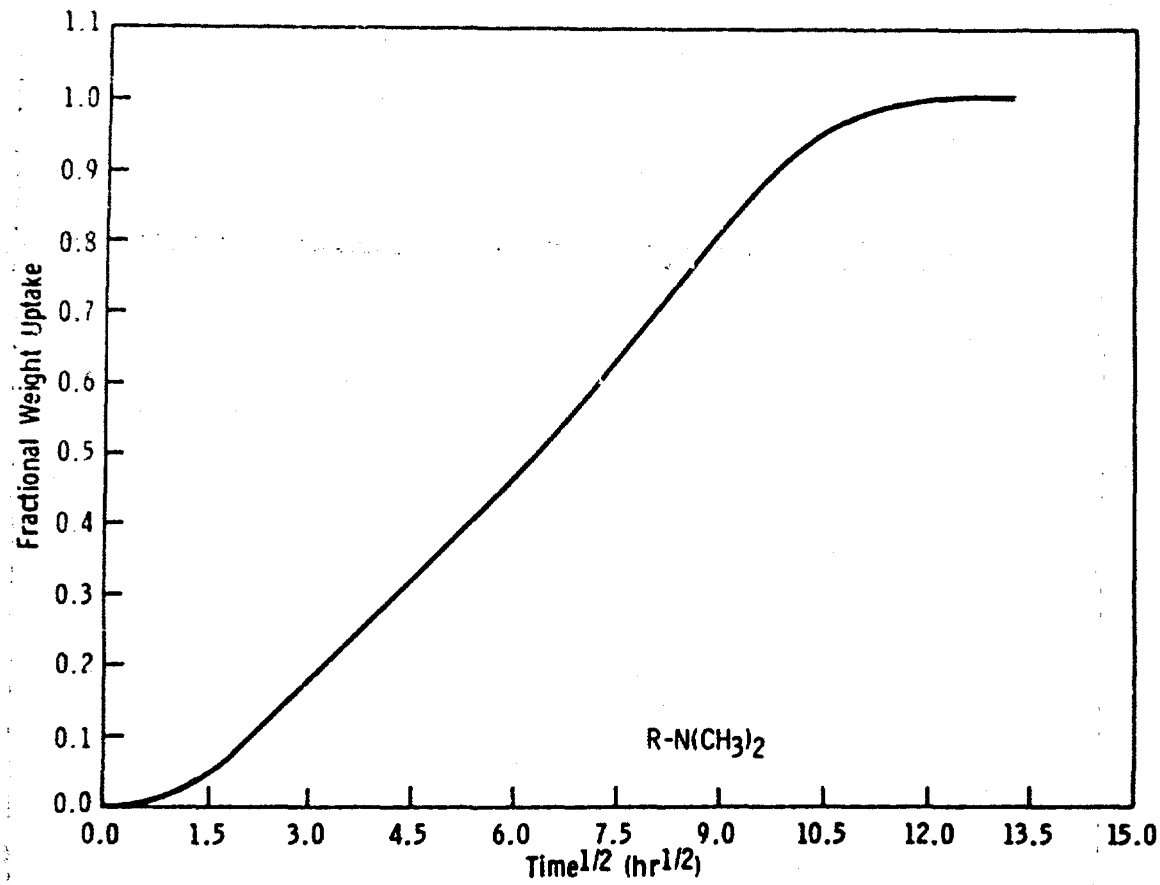


Figure 3. Vapor sorption of 1-decanol into dye 3-containing polyurethane.

Fluorescence Microscopy

Samples exhibited an even distribution of fluorescence intensity across the length and width. A dye 3-containing sample that had been treated with methyl benzilate exhibited significantly brighter fluorescence than its untreated counterpart. No crystallites of any kind were observed in the treated sample. This indicates that the polymer samples used in the experiments discussed above were free of large precipitated dye crystals, which would cause tremendous variability among samples.

SUMMARY

The 1,3-indanedione-1-imine dyes were found to form molecular complexes with certain aliphatic and aromatic compounds when immobilized on either an inorganic support or in a polyurethane matrix. Complex formation was identified by the increase in fluorescence of these dyes and the dye-containing polyurethanes. The fluorescence response depended on the method by which the organic molecule was introduced into the polyurethane. When methyl benzilate 12 was introduced by immersion or adsorption, the dye 3-containing system exhibited greater fluorescence enhancement; however, when 12 was introduced during polymerization, the dye 7-labeled system exhibited greater fluorescence. Fluorescence enhancement in the presence of an aliphatic compound occurred in a vapor sorption experiment on a polymer film containing 3.

ACKNOWLEDGEMENT

The authors thank Dr. William Eldrid of the Department of Biology, Boston University, for the very generous use of his Olympus Vanox epi-fluorescence microscope.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: SLCIS-IM-TL
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22314
1	ATTN: DTIC-FDAC
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCLD
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
	Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703
1	ATTN: AMDSD-L
1	AMDSD-E
	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35898
1	ATTN: AMSMI-RKP, J. Wright, Bldg. 7574
1	AMSMI-TB, Redstone Scientific Information Center
1	AMSMI-RLM
1	Technical Library
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
1	ATTN: Technical Library
1	AMDAR-QAC-E
1	AMDAR-LCA, Mr. Harry E. Pebly, Jr., PLASTEC, Director
	Commander, U.S. Army Natick Research, Development, and Engineering Center, Natick, MA 01760
1	ATTN: Technical Library
	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library

No. of Copies	To
	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
	President, Airborne Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library
	Director, U.S. Army Ballistics Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: AMDAR-TSB-S (STINFO)
	Commander, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD 21010
1	ATTN: SMCCR-RSC-C, W. Shuely
1	AMCCR-RSP-C, W. P. Ashman
1	SMCCR-RS, E. J. Poziomek
	Commander, Dugway Proving Ground, Dugway, UT 84022
1	ATTN: Technical Library, Technical Information Division
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: Technical Information Office
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, Charlottesville, VA 22901
1	ATTN: Militray Tech
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library
	Director, Eustis Directorate, U.S. Army Air Mobility Research and Development Laboratory, Fort Eustis, VA 23604-5577
1	ATTN: SAVDL-E-MOS (AVSCOM)
	Commander, Naval Research Laboratory, Washington, DC 20375
1	ATTN: Dr. G. R. Yoder - Code 6384
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
	Edward J. Morrissey, Wright-Patterson Air Force Base, OH 45433
1	ATTN: AFWAL/MLTE
	Commander, U.S. Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, OH 45433
1	ATTN: AFWAL/MLC
1	AFWAL/MLLP, M. Forney, Jr.
1	AFWAL/MLBC, Mr. Stanley Schulman

No. of Copies	To
	U.S. Department of Commerce, National Bureau of Standards, Gaithersburg, MD 20899
1	ATTN: Chief, Polymer Division, Institute for Materials Science and Engineering
	National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, AL 35812
1	ATTN: R. J. Schwinghammer, EH01, Dir., M&P Lab
	U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1	ATTN: Technical Library
	Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916
1	ATTN: Technical Library
	Commander, U.S. Army Engineer School, Fort Belvoir, VA 22060
1	ATTN: Library
	Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180
1	ATTN: Research Center Library
	Technical Director, Human Engineering Laboratories, Aberdeen Proving Ground, MD 21005
1	ATTN: Technical Reports Office
	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1	ATTN: Quartermaster School Library
	Commander, Naval Research Laboratory, Washington, DC 20375
1	ATTN: Dr. C. I. Chang - Code 5830
	National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, AL 35812
1	ATTN: Mr. W. A. Wilson, EH41, Bldg. 4612
1	Committee on Marine Structures Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418
	U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
1	ATTN: SLCMT-IML
4	Authors

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
FLUORESCENCE ENHANCEMENT IN A POLYURETHANE
CONTAINING AN ORGANIC DYE -
Orna I. Kutal, Samuel J. Huang,
Catherine A. Byrne, and Edward J. Poziomek

Technical Report MTL TR 87-45, September 1987, 14 pp -
illus-tables

AD ________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Fluorescence
Polyurethanes
Azine fluorescence

Transparent polyurethane sheets have been prepared containing a dispersed or covalently bonded organic dye. The fluorescent dyes are 2-diphenylacetyl-1,3-indanedione-1-p-dimethylaminobenzaldazine or the p-dihydroxyethylaminobenzaldazine analog, which can be called DIPAIN derivatives. Changes in the fluorescence of the dyes have been studied in the presence of methyl benzilate and several nonvolatile aliphatic alcohols. When methyl benzilate is added during polymerization, fluorescence in both dye-containing sheets increases, but the effect is greater for the sheet containing the covalently bonded dye. When a solution of methyl benzilate is dropped on the surfaces of the dye-containing sheets, the effect is greater for the dispersed dye. The dimethyl dye blooms to the surface of the polyurethane sheet and can be wiped off as a fine orange powder. Decyl alcohol shows an enhancement effect when spotted together with the dimethyl dye on a silica gel TLC plate. Fluorescence enhancement is also observed when a polyurethane sheet containing dimethyl dye is placed in contact with decyl alcohol vapor. The nature of the interaction can include the aromatic ring systems of the dye and methyl benzilate, and also the interaction of the dye with decyl alcohol through hydrogen bonding.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
FLUORESCENCE ENHANCEMENT IN A POLYURETHANE
CONTAINING AN ORGANIC DYE -
Orna I. Kutal, Samuel J. Huang,
Catherine A. Byrne, and Edward J. Poziomek

Technical Report MTL TR 87-45, September 1987, 14 pp -
illus-tables

AD ________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Fluorescence
Polyurethanes
Azine fluorescence

Transparent polyurethane sheets have been prepared containing a dispersed or covalently bonded organic dye. The fluorescent dyes are 2-diphenylacetyl-1,3-indanedione-1-p-dimethylaminobenzaldazine or the p-dihydroxyethylaminobenzaldazine analog, which can be called DIPAIN derivatives. Changes in the fluorescence of the dyes have been studied in the presence of methyl benzilate and several nonvolatile aliphatic alcohols. When methyl benzilate is added during polymerization, fluorescence in both dye-containing sheets increases, but the effect is greater for the sheet containing the covalently bonded dye. When a solution of methyl benzilate is dropped on the surfaces of the dye-containing sheets, the effect is greater for the dispersed dye. The dimethyl dye blooms to the surface of the polyurethane sheet and can be wiped off as a fine orange powder. Decyl alcohol shows an enhancement effect when spotted together with the dimethyl dye on a silica gel TLC plate. Fluorescence enhancement is also observed when a polyurethane sheet containing dimethyl dye is placed in contact with decyl alcohol vapor. The nature of the interaction can include the aromatic ring systems of the dye and methyl benzilate, and also the interaction of the dye with decyl alcohol through hydrogen bonding.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
FLUORESCENCE ENHANCEMENT IN A POLYURETHANE
CONTAINING AN ORGANIC DYE -
Orna I. Kutal, Samuel J. Huang,
Catherine A. Byrne, and Edward J. Poziomek

Technical Report MTL TR 87-45, September 1987, 14 pp -
illus-tables

AD ________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Fluorescence
Polyurethanes
Azine fluorescence

Transparent polyurethane sheets have been prepared containing a dispersed or covalently bonded organic dye. The fluorescent dyes are 2-diphenylacetyl-1,3-indanedione-1-p-dimethylaminobenzaldazine or the p-dihydroxyethylaminobenzaldazine analog, which can be called DIPAIN derivatives. Changes in the fluorescence of the dyes have been studied in the presence of methyl benzilate and several nonvolatile aliphatic alcohols. When methyl benzilate is added during polymerization, fluorescence in both dye-containing sheets increases, but the effect is greater for the sheet containing the covalently bonded dye. When a solution of methyl benzilate is dropped on the surfaces of the dye-containing sheets, the effect is greater for the dispersed dye. The dimethyl dye blooms to the surface of the polyurethane sheet and can be wiped off as a fine orange powder. Decyl alcohol shows an enhancement effect when spotted together with the dimethyl dye on a silica gel TLC plate. Fluorescence enhancement is also observed when a polyurethane sheet containing dimethyl dye is placed in contact with decyl alcohol vapor. The nature of the interaction can include the aromatic ring systems of the dye and methyl benzilate, and also the interaction of the dye with decyl alcohol through hydrogen bonding.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
FLUORESCENCE ENHANCEMENT IN A POLYURETHANE
CONTAINING AN ORGANIC DYE -
Orna I. Kutal, Samuel J. Huang,
Catherine A. Byrne, and Edward J. Poziomek

Technical Report MTL TR 87-45, September 1987, 14 pp -
illus-tables

AD ________

UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words

Fluorescence
Polyurethanes
Azine fluorescence

Transparent polyurethane sheets have been prepared containing a dispersed or covalently bonded organic dye. The fluorescent dyes are 2-diphenylacetyl-1,3-indanedione-1-p-dimethylaminobenzaldazine or the p-dihydroxyethylaminobenzaldazine analog, which can be called DIPAIN derivatives. Changes in the fluorescence of the dyes have been studied in the presence of methyl benzilate and several nonvolatile aliphatic alcohols. When methyl benzilate is added during polymerization, fluorescence in both dye-containing sheets increases, but the effect is greater for the sheet containing the covalently bonded dye. When a solution of methyl benzilate is dropped on the surfaces of the dye-containing sheets, the effect is greater for the dispersed dye. The dimethyl dye blooms to the surface of the polyurethane sheet and can be wiped off as a fine orange powder. Decyl alcohol shows an enhancement effect when spotted together with the dimethyl dye on a silica gel TLC plate. Fluorescence enhancement is also observed when a polyurethane sheet containing dimethyl dye is placed in contact with decyl alcohol vapor. The nature of the interaction can include the aromatic ring systems of the dye and methyl benzilate, and also the interaction of the dye with decyl alcohol through hydrogen bonding.